

The basics.

$f(C_i) dV_c =$ fraction of molecules in class C_i , i.e.
 fraction with velocity in the range $(C_i, C_i + dC_i)$

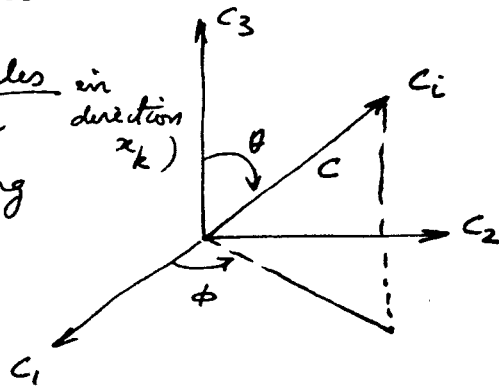
C_i is a vector $C_i \equiv (C_1, C_2, C_3)$

$$dV_c = dC_1 dC_2 dC_3 \quad \text{Cartesian}$$

$$= C^2 dC \sin\theta d\theta d\phi \quad \text{Spherical polar}$$

Representation of dV_c depends on coordinate basis chosen in velocity space

Flux of molecules $\phi_k^{(n)}$ ($\frac{\# \text{ of molecules in direction } x_k}{\text{time area}}$)
Differential flux of molecules traveling in direction k : $d^{(3)} \phi_k^{(n)}$



$$d^{(3)} \phi_k^{(n)} = n (C_i \cdot \hat{i}_k) f(C_i) dV_c$$

e.g. differential flux in x_2 direction $d^{(3)} \phi_2^{(n)} = n C_2 f(C_i) dV_c$

Note that C_2 is the x_2 -component of velocity C_i , & $d^{(3)} \phi_2^{(n)}$ is the differential flux of molecules of class C_i in the x_2 direction.

One can construct differential fluxes of momentum and energy. Number flux and energy flux are ~~sc~~ vectors - the direction is the direction in which transport occurs. Momentum flux is a tensor - one "direction" is the momentum component and the other is the direction in which this vector quantity is being transported.

e.g. (1) $d^{(3)} \phi_2^{(E)} = \frac{1}{2} m C^2 n C_2 f(C_i) dV_c$ - differential kinetic energy flux in x_2 -direction being transported by molecules of class C_i

$\frac{1}{2} m C^2$ is KE of molecules of class C_i

C_2 is $C_i \cdot \hat{i}_2$ x_2 -comp x_2 -component of C_i

(2) $d^{(3)} \phi_{12}^{(p)} = m C_1 n C_2 f(C_i) dV_c$ - differential x_1 -momentum flux in x_2 -direction transported by molecules of class C_i

Collisions occur constantly and tend to change the velocity distribution because velocities emerging from a collision are different from velocity entering a collision: $(c_i, z_i) \rightarrow (c_i', z_i')$

The equilibrium distribution is the one that remains unchanged even though collisions continue to occur.

Collision rate $Z_{AB} = \frac{\# \text{ of collisions}}{\text{time vol}}$ between molecules

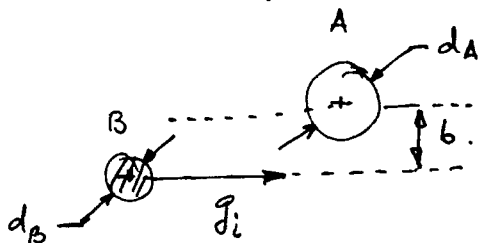
of type A and molecules of type B.

For a model of molecules as tiny hard spheres or "billiard balls" a collision event is not very definite. In the real (quantum) world of nuclei surrounded by swarms of electrons things are not so clear cut and one is reduced to defining probabilities of particular outcomes given specified inputs.

First taking a hard sphere (HS) approach, consider a molecule of type A of class c_i and a molecule type B of class z_i .

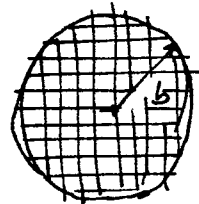
A & B have masses m_A, m_B and diameters d_A & d_B respectively

The velocity of B relative to A, $g_i \equiv z_i - c_i$



For hard spheres, it is obvious that a collision occurs if

$$b \leq \frac{d_A + d_B}{2} \equiv d_{AB}$$



One can imagine a sphere of radius d_{AB} surrounding the centre of A. If the trajectory of any B molecule brings its centre inside this sphere a collision will occur between A & B. The cross-section of this sphere is a target area & if the relative velocity g_i is directed ~~to~~ inside this target collision will occur. This area is called the collision cross section. σ_T (total collision cross-section).

For hard spheres: $\sigma_T = \pi d_{AB}^2$

For many gas dynamic calculations this simple model is not accurate enough (though it predicts things qualitatively).

The variable hard sphere (VHS) model improves on the HS model by using $\sigma_T = \sigma(g)$ where g is the relative speed, i.e. the magnitude of g_i . This is the current state-of-the-art for most aerodynamics calculations. For chemistry and physics vastly more complicated models are used.

The cross-section above was called total because it sums (or integrates) over all possible outcomes of the collision, i.e., for elastic collisions, over all possible c_i', z_i' consistent with c_i & z_i (& hence g_i).

[For the most general type of collision, the total cross-section includes the possibility that "anything" has happened and thus includes a sum of probability of a reaction, or inelastic collision or elastic collision].

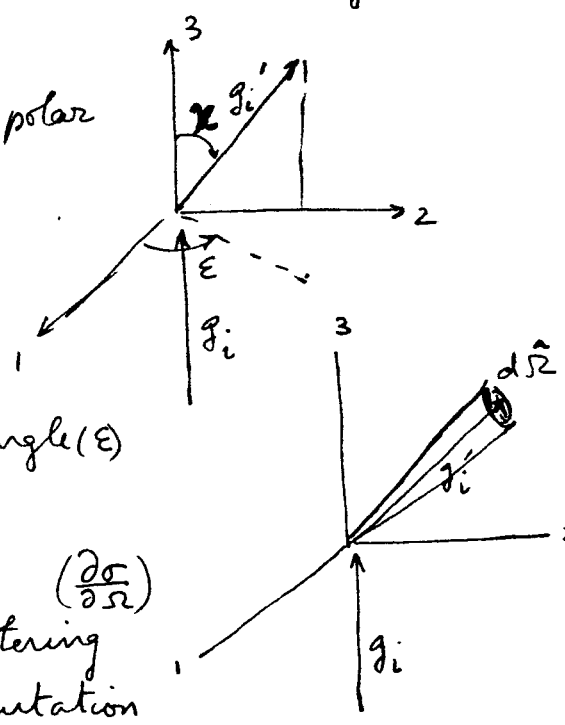
For restricting ourselves to elastic collisions for the moment [Elastic \Leftrightarrow no change in molecular internal energy, kinetic energy constant]

then conservation of momentum & energy shows $g' = g$
 i.e. relative speed after collision = relative speed before collision.
 Note however $g_i' \neq g_i$ i.e. ^{relative} velocity can change.

Elastic collisions change the direction (but not the magnitude) of the relative velocity vector

The scattering can be specified by the polar angles χ, ϵ that indicate the orientation of g_i' relative to g_i

The differential scattering solid angle $d\hat{\Omega}$ corresponding to small variations in polar angle (χ) and azimuthal angle (ϵ) is given by $d\hat{\Omega} = \sin \chi d\chi d\epsilon$.



The differential scattering cross-section $(\frac{\partial \sigma}{\partial \hat{\Omega}})$ corresponds to the probability that scattering occurs into $d\hat{\Omega}$, i.e. that g_i' has orientation (χ, ϵ) or within $d\chi, d\epsilon$ of (χ, ϵ)

The total cross-section
$$\sigma_T = \int_{\hat{\Omega}} \left(\frac{\partial \sigma}{\partial \hat{\Omega}}\right) d\hat{\Omega} = \int_{\epsilon=0}^{2\pi} \int_{\chi=0}^{\pi} \left(\frac{\partial \sigma}{\partial \hat{\Omega}}\right) \sin \chi d\chi d\epsilon$$

If the scattering is azimuthally symmetric (independent of ϵ):

then
$$\sigma_T = 2\pi \int_{\chi=0}^{\pi} \left(\frac{\partial \sigma}{\partial \hat{\Omega}}\right) \sin \chi d\chi$$

If the scattering is totally isotropic (independent of both χ & ϵ)

then
$$\sigma_T = 4\pi \left(\frac{\partial \sigma}{\partial \hat{\Omega}}\right)$$

(Isotropic scattering is commonly assumed in aerodynamic calculations using Monte Carlo methods but it is not very realistic)

Hard spheres are isotropic scatterers. Using $\sigma_T = \pi d_{AB}^2$, we get

$$\left(\frac{\partial \sigma}{\partial \hat{\Omega}}\right)_{HS} = d_{AB}^2 / 4$$

Using the cross-section ideas one can write down the differential collision rate for molecules A of class C_i with molecules B of class Z_i .

Consider first a single B molecule of class Z_i . Then it is moving at speed g_i relative to A molecules of class C_i and "sweeps a volume" $dV = g dt \cdot \left(\frac{\partial \sigma}{\partial \Omega}\right) d\hat{\Omega}$ in time dt .

distance area

The number of A molecules of class C_i in this volume is

$$n_A f_A(C_i) dV_C \cdot g dt \left(\frac{\partial \sigma}{\partial \Omega}\right) d\hat{\Omega},$$

so the ~~class~~ differential collision frequency for ^{a single} this B molecule of class Z_i

$$d^{(5)} \theta_{BA} = n_A f_A(C_i) dV_C \cdot g \left(\frac{\partial \sigma}{\partial \Omega}\right) d\hat{\Omega}$$

But there are $n_B f_B(Z_i) dV_Z$ such B molecules per unit volume so

$$d^{(8)} Z_{BA} = d^{(8)} Z_{AB} = n_A f_A(C_i) dV_C \cdot n_B f_B(Z_i) dV_Z \cdot g \left(\frac{\partial \sigma}{\partial \Omega}\right) d\hat{\Omega}$$

(A colliding with B is the same as B colliding with A).

To get macroscopic rate one has to do the required integrations.

One can immediately integrate over all $d\hat{\Omega}$

$$d^{(6)} Z_{AB} = n_A f_A(C_i) dV_C \cdot n_B f_B(Z_i) dV_Z \cdot g \sigma_T$$

where we use $\sigma_T = \int_{\Omega} \frac{\partial \sigma}{\partial \Omega} d\hat{\Omega}$, and note that

$$\sigma_T = \sigma_T(g) \text{ in general.}$$

The Maxwell distribution is obtained by requiring detailed balance on depleting & replenishing rates. Replenishing rates are most easily handled by using the concept of inverse collisions.

The inverse collision $(C_i', Z_i') \rightarrow (C_i, Z_i)$ is paired with the direct collision $(C_i, Z_i) \rightarrow (C_i', Z_i')$ which is a depleting collision.

$$\text{Then } \frac{\partial}{\partial t} \left[n_A f_A(C_i) dV_c \right]_{\text{colls}} = n_A n_B \int_{V_z} \int_{\hat{\Omega}} \left[f_A(C_i') f_B(Z_i') - f_A(C_i) f_B(Z_i) \right] g \left(\frac{\partial \sigma}{\partial R} \right) d\hat{\Omega} dV_z d'$$

where we have used (without proof) that $\left(\frac{\partial \sigma}{\partial R} \right) d\hat{\Omega} \Big|_{\text{direct}} = \left(\frac{\partial \sigma}{\partial R} \right) d\hat{\Omega}' \Big|_{\text{inver}}$

$$dV_z, dV_{c'} = dV_z dV_c.$$

Recall that $g' = g$ for elastic collisions.

Detailed balance requires that the equilibrium condition

$$\frac{\partial}{\partial t} \left[n_A f_A(C_i) dV_c \right]_{\text{colls}} = 0$$

is satisfied not because the integral $\int_{V_z} \int_{\hat{\Omega}} [] d\hat{\Omega} dV_z = 0$

but because the integrand is zero. Thus $f_A(C_i') f_B(Z_i') = f_A(C_i) f_B(Z_i)$

As shown in the text this leads ultimately to the equilibrium (Maxwellian) distribution

$$f_m(C_i) dV_c = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mC^2}{2kT}} dV_c.$$

where $m = m_A$ or m_B (as req'd) and C_i is a dummy variable (could be Z_i too!)

Maxwellian velocity distribution $f_M(c_i) dV_c = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m c^2}{2kT}} dV_c$.

Maxwellian speed distribution $\chi_M(c) dc$.

$$\chi_M(c) dc = \int_{\text{orientations of } c_i} f_M(c_i) dV_c = 4\pi c^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m c^2}{2kT}} dc.$$

Showed in class that if a gas had two components A & B each of which was Maxwellian distributed (i.e. with parameter T, i.e. each of which was at equilibrium at temp. T, then for pairs AB selected at random the relative velocity distribution function $f(g_i)$ is also Maxwellian, and is characterized by temp. T and reduced mass $m_{AB}^* = \frac{m_A m_B}{m_A + m_B}$.

$$f(g_i) = f_M(g_i) = \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} e^{-\frac{m_{AB}^* g^2}{2kT}} dV_g.$$

The relative speed distribution $\chi_M(g) dg = \int_{\text{orientations of } g_i} f_M(g_i) dV_g$

$$= \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} e^{-\frac{m_{AB}^* g^2}{2kT}} 4\pi g^2 dg$$

These results can be used to simplify the expression for $d^{(6)}Z_{AB}$ in the case that $f_A(c_i)$ & $f_B(z_i)$ are Maxwellian.

$$d^{(6)}Z_{AB} = n_A f_A(c_i) n_B f_B(z_i) g \sigma_T(g) dV_c dV_z.$$

transform to centre of mass frame $c_i = G_i - \frac{m_{AB}^*}{m_A} g_i$

$$z_i = G_i + \frac{m_{AB}^*}{m_B} g_i$$

$$g_i \equiv z_i - c_i$$

$$G_i \equiv \frac{m_A c_i + m_B z_i}{m_A + m_B}$$

One gets finally after integrating over all ξ_i :

$$\begin{aligned} dZ_{AB} &= n_A n_B \left(\frac{m_{AB}^*}{2\pi kT} \right)^{3/2} e^{-\frac{m_{AB}^* g^2}{2kT}} 4\pi g^2 \cdot g \sigma_T(g) dg \\ &= n_A n_B g \sigma_T(g) \chi_M(g) dg. \end{aligned}$$

One can now pose the question: What is the relative speed distribution of molecules that collide? This should be contrasted to the question result obtained earlier for the relative speed distribution for molecules chosen at random. The specification that the molecules collide changes the result (in general) because one is now answering a different question.

Let us call the relative speed distribution of colliding molecules $\chi_c(g)$.

Then by definition of a distribution fn.

$$\begin{aligned} \chi_c(g) dg &\equiv \text{fraction of molecules that collide with speeds in} \\ &\quad \text{the range } (g, g+dg). \\ &= \frac{\# \text{ of collisions per unit vol with speeds in range } (g, g+dg)}{\# \text{ of collisions per unit vol.}} \\ &= \frac{dZ_{AB}}{Z_{AB}}. \end{aligned}$$

$$\text{Thus } \chi_c(g) dg = \frac{n_A n_B g \sigma_T(g) \chi_M(g) dg}{n_A n_B \int_0^{\infty} g \sigma_T(g) \chi_M(g) dg}$$

$$\chi_c(g) dg = \frac{g \sigma_T(g) \chi_M(g) dg}{\int_0^\infty g \sigma_T(g) \chi_M(g) dg}$$

We see immediately that even if $\sigma_T = \text{const}$, independent of g corresponding to HS, then

$$\chi_c^{HS}(g) dg = \frac{g \chi_M(g) dg}{\int_0^\infty g \chi_M(g) dg} = \frac{g \chi_M(g) dg}{\bar{g}}$$

$$\bar{g} = \left(\frac{8kT}{\pi m_{AB}^*} \right)^{1/2} ;$$

$$\chi_c^{HS}(g) dg \neq \chi_M(g) dg \quad \text{i.e.} \quad \chi_c^{HS}(g) \neq \chi_M(g)$$

the relative speed distribution for colliding molecules is not the same as $\chi_M(g)$ the relative speed distribution of molecules chosen at random.

Explicitly:

$$\begin{aligned} \chi_c^{HS}(g) dg &= g \cdot \left(\frac{\pi m_{AB}^*}{8kT} \right)^{1/2} \cdot \left(\frac{m_{AB}^*}{2\pi kT} \right)^{3/2} e^{-\frac{m_{AB}^* g^2}{2kT}} \cdot 4\pi g^2 dg \\ &= \frac{1}{2} \left(\frac{m_{AB}^*}{kT} \right)^2 e^{-\frac{m_{AB}^* g^2}{2kT}} g^3 dg \end{aligned}$$

Verify normalization

$$\begin{aligned} \int_0^\infty \chi_c^{HS}(g) dg &= \frac{1}{2} \left(\frac{m_{AB}^*}{kT} \right)^2 \int_0^\infty e^{-\frac{m_{AB}^* g^2}{2kT}} g^3 dg \\ &= \frac{1}{2} \left(\frac{m_{AB}^*}{kT} \right)^2 \cdot \frac{1}{2} \left(\frac{2kT}{m_{AB}^*} \right)^2 \\ &= 1 \quad \text{as required.} \end{aligned}$$

For the special case $\sigma_T(g) = \frac{K}{g}$ $K = \sigma_0 g_{ref}$.

$$\text{then } \chi_c(g) dg = \frac{\int \frac{K}{g} \chi_M(g) dg}{\int_0^\infty \frac{K}{g} \chi_M(g) dg} = \frac{\chi_M(g) dg}{\int_0^\infty \chi_M(g) dg} = \chi_M(g) dg.$$

Only in this case $\chi_c(g) dg = \chi_M(g) dg$. Such molecules are called "Maxwellian" molecules. Use of $\sigma_T(g) = \frac{K}{g}$ simplifies many calculation & Maxwell made extensive use of this model. It may be shown [Chap IX, secs 8, 9] that to bear have $\sigma_T(g) = \frac{K}{g}$ molecules must have an inverse power repulsive potential $V(r)$ that varies as $V(r) \sim \frac{1}{r^\alpha}$. Hard sphere molecules behave (in a certain limit) as though $V(r) \sim \frac{1}{r^\alpha}$ $\alpha \rightarrow \infty$. Looking at the behavior of real gases it is found that the hard sphere model is "too hard" whereas the Maxwell molecules are too "soft". This statement is based on the temperature dependence of the coefficient of viscosity (μ).

Solutions of the Boltzmann equation for inverse power model cross-sections (see chap IX) show that $\mu = \mu_{ref} \left(\frac{T}{T_{ref}}\right)^{\frac{1}{2} + \frac{2}{\alpha}}$

where $V \sim \frac{1}{r^\alpha}$. Thus for HS. ($\alpha \rightarrow \infty$) $\mu = \mu_{ref} \left(\frac{T}{T_{ref}}\right)^{1/2}$,

whereas for Maxwell molecules ($\alpha = 4$) $\mu = \mu_{ref} \left(\frac{T}{T_{ref}}\right)$

The temperature dependence of μ for N_2 (for example) suggests $\alpha = 9-11$. Note, however, that an inverse power model for N_2-N_2 interactions is by no means a perfect model though it works for many aerodynamic calculations.

For the more general case $\sigma_T(g) = \sigma_{ref} \left(\frac{g}{g_{ref}} \right)^{-\omega}$

VHS model.

Variable hard
sphere.

Negative sign
usually explicit

$$\begin{aligned} \chi_c(g) dg &= \frac{g \cdot \left(\frac{g}{g_{ref}} \right)^{-\omega} \chi_M(g) dg}{\int_0^{\infty} g \left(\frac{g}{g_{ref}} \right)^{-\omega} \chi_M(g) dg} \\ &= \frac{g^{1-\omega} \chi_M(g) dg}{\int_0^{\infty} g^{(1-\omega)} \chi_M(g) dg} = \frac{g^{3-\omega} e^{-\frac{m^* g^2}{2kT}} dg}{\int_0^{\infty} g^{3-\omega} e^{-\frac{m^* g^2}{2kT}} dg} \end{aligned}$$

Using the result for the gamma function from the handout:

$$\int_0^{\infty} v^n e^{-\beta v^2} dv = \frac{1}{2} \beta^{-\frac{n+1}{2}} \Gamma\left(\frac{n+1}{2}\right)$$

(complete) Γ fn rather
than incomplete Γ fn
because lower limit of
integration is 0.

So $\int_0^{\infty} g^{3-\omega} e^{-\frac{m^* g^2}{2kT}} dg$ has $n = 3 - \omega$
 $\beta = \frac{m^*}{2kT}$

$$= \frac{1}{2 \left(\frac{m^*}{2kT} \right)^{\frac{4-\omega}{2}}} \Gamma\left(\frac{4-\omega}{2}\right).$$

Finally $\chi_c(g) dg = 2 \left(\frac{m^*}{2kT} \right)^{\frac{4-\omega}{2}} \frac{1}{\Gamma\left(\frac{4-\omega}{2}\right)} g^{3-\omega} e^{-\frac{m^* g^2}{2kT}} dg$

Change of variable.

Ex. Kinetic energy distribution function.

Let ϵ be KE. & $F(\epsilon)d\epsilon$ = fraction of molecules with KE in range $(\epsilon, \epsilon+d\epsilon)$.

Want an explicit expression for $F(\epsilon)d\epsilon$.

Now $\epsilon = \frac{1}{2} m C^2$ so could (should!) use speed distribution function $X(C)dC = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mC^2}{2kT}} dC \cdot 4\pi C^2$

$$\begin{aligned} \epsilon &= \frac{1}{2} m C^2 & d\epsilon &= m C dC & dC &= \frac{d\epsilon}{mC} \\ C &= \left(\frac{2\epsilon}{m}\right)^{1/2} & C^2 &= \frac{2\epsilon}{m} \end{aligned}$$

Fraction in range $(\epsilon, \epsilon+d\epsilon)$

$$X(C)dC = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{\epsilon}{kT}} \frac{d\epsilon}{m} \left(\frac{2\epsilon}{m}\right)^{-1/2} \cdot 4\pi \left(\frac{2\epsilon}{m}\right)$$

$$= \left(\frac{m}{2\pi kT}\right)^{1/2} \cdot \left(\frac{m}{2\pi kT}\right) \cdot \frac{4\pi}{m} \left(\frac{2\epsilon}{m}\right)^{1/2} e^{-\epsilon/kT} d\epsilon$$

$$= 2 \left(\frac{\epsilon}{\pi kT}\right)^{1/2} e^{-\epsilon/kT} \frac{d\epsilon}{kT} = \frac{2}{\sqrt{\pi}} \left(\frac{\epsilon}{kT}\right)^{1/2} e^{-\epsilon/kT} \frac{d\epsilon}{kT}$$

By definition this is: $F(\epsilon)d\epsilon = \frac{2}{\sqrt{\pi}} \left(\frac{\epsilon}{kT}\right)^{1/2} e^{-\epsilon/kT} \frac{d\epsilon}{kT}$

check normalization $\int_0^{\infty} F(\epsilon)d\epsilon = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \left(\frac{\epsilon}{kT}\right)^{1/2} e^{-\epsilon/kT} \frac{d\epsilon}{kT}$

let $\frac{\epsilon}{kT} = x$ $dx = \frac{d\epsilon}{kT}$

$$\int_0^{\infty} F(\epsilon)d\epsilon = \frac{2}{\sqrt{\pi}} \int_0^{\infty} x^{1/2} e^{-x} dx = \frac{2}{\sqrt{\pi}} \int_0^{\infty} x^{3/2-1} e^{-x} dx$$

$$= \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}\right) = \frac{2}{\sqrt{\pi}} \cdot \frac{1}{2} \Gamma\left(\frac{1}{2}\right) = \frac{2}{\sqrt{\pi}} \cdot \frac{1}{2} \cdot \sqrt{\pi} = 1$$

as required